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Study of the Properties of Micelles

FINAL REPORT

by
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Preface

During the past decade, the field of surface chemistry
has been enriched by the contributions emanating from
Professor Mysels' laboratory at the University of Southern
California. The highest order of experimental accuracy
and reliability, not divorced from great insight into the
nature of surface phenomena, have characterized the work
of that laboratory.   Lloyd Ossipov, reviewer of Soap
Films in J. Chem. Ed., 37, 820 (1960)

These kind words of a reviewer do not point out that the bulk of

the work referred to was made possible by the ONR contract for which this

is the final report. I am, however, very much aware of this fact and

realize that without this sustained support my efforts would have been

much less productive, and my students and coworkers would not have been

able to develop to the extent they did.

It is therefore fitting to begin this report by an expression of

sincere gratitude to the organization and the responsible individuals

in it.

Introduction

This report summarizes the work accomplished under Contract
Nonr-274(000), Project NR356-254 (formerly NR054-254) during its lifetime
from April 1, 1951 to November 30, 1961. The first section (pp. 2-16) gives
a brief summary of the scientific results, the second section (pp. 17-19)
deals with the personnel involved in it, the third section (pp. 20-22)
lists the scientific publications, and the fourth section (pp. 23-24) the
technical reports.

I. SCIENTIFIC RESULTS

Introduction[*]

Work under this contract began a decade ago. At that time it was well established that solutions of association colloids formed micelles at high concentration, it was generally believed that at low concentrations they behaved as simple one-one electrolytes, while these two regimes were separated by a relatively uncertain critical region. The size, shape and structure of the micelle were subjects of controversy between extreme views, and almost nothing was known about its charge. Except for the light scattering method which had been just developed by Debye, there were no techniques for observing the behavior of micelles themselves, and theoretical interpretations were in terms of first and very rough approximations.

Today the situation is very different. The methods for measuring the properties of micelles have been greatly improved and their interpretation is much more sophisticated. As a result rather narrow limits can be placed on their size, charge, shape and structure for those systems that have been studied in detail and it is only a matter of time and effort to obtain this type of information for other systems. Methods of studying the region of the critical micelle concentration have also been improved and their limitations have been understood so that this region too is quite well understood. In contrast, the dilute solutions now appear more complicated than was believed earlier and there is considerable disagreement as to their nature. This in turn introduces an uncertainty into the final details of interpreting measurements on micelles and on the critical micelle concentration and affects much of the theoretical interpretation in terms of forces governing the formation of micelles.

Thus considerable progress has been made, but the total picture is still not completely clear. This progress has been the result of contributions from many laboratories and many workers. The following will briefly summarize the part played by work under this project.

Methods and Techniques

1. <u>Tracer methods</u>. Our original reason for entering the study of association colloids was the conception of the tracer method for the study of micelles.[*] It involves the use of water-insoluble dyes which are slightly soluble in micelles. Thus, the dye has to always remain in a micelle and move with it. By observing the motion of the dye one observes therefore the motion of the micelle. Because it is only seldom that more than one dye molecule is dissolved in a micelle, the properties of the micelles are not changed appreciably, and since the dye is completely hydrophobic, it stays inside the micelle and does not affect its surface. This method of "painting the micelle red in order to follow its movement" has been applied to electrophoresis and to diffusion.

In case of <u>electrophoresis</u> a completely new approach had to be used because of the absence of stabilizing density differences present in conventional methods. The apparatus developed (2) is very simple and its accuracy is limited mainly by that of the analytical determination of the tracer. It can be used not only with micelles tagged by the above method but also with the more conventional radioactive tracers either for simple ions or large colloidal particles. The method has been used by us in the study of the electrophoretic mobility of micelles (2) and their

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[*] H. W. Hoyer, and K. J. Mysels, "A Method for Determining the Properties of Micelles," J. Phys. and Colloid Chem., 54, 966 (1950).
Also, K. J. Mysels, "Tagging the Elusive Micelle," Research Reviews (Office of Naval Research), September, 1953, p. 15.

counterions (6) in sodium lauryl sulfate. It has been used later by Professor Hoyer for similar determinations on a variety of micelles[*] and also in our laboratory for the study of human serum albumin under a variety of conditions not accessible to conventional methods.[**] In addition to its simplicity, this "open tube" tracer electrophoresis method has the advantages of completely eliminating so-called boundary anomalies which introduce some uncertainty into more conventional moving boundary methods, of being applicable over a much wider range of concentrations and ionic strengths, and of being usable without complications over a wide range of temperatures. In the study of micelles it has the clear advantage of measuring only the electrophoretic mobility of micelles and not being influenced by the mobility of either any supporting electrolytes present or the non-micellized components.

We also developed another tracer electrophoresis method (5) which was an improvement over a method published by Brady and involved, like his, the use of a fritted glass disc. Because of the ever-present problem of the possible disturbing effect of the large surface of the frit, we have used this method only to check the open tube method and did indeed obtain concordant results.

In order to study the self diffusion of tagged micelles we developed a new method for measuring diffusion coefficients using sintered glass discs to immobilize the liquid (1). This turned out to be useful not only for tracer systems, but also for those using a concentration gradient. While somewhat tedious, the method is perhaps the best one available for measuring the self diffusion of particles having a low diffusion coefficient. It is also perhaps the most direct, and quite an accurate one, for measuring their diffusion coefficient with a concentration gradient. However, it can be used only with systems which are not affected by the large glass surface present in the frit. Unfortunately, it turned out later (9) that the particular system for which we used it, namely, sodium lauryl

[*] H. W. Hoyer and A. Greenfield, J. Phys. Chem., 61, 735 (1957); H. W. Hoyer, A. Marmo and M. Zoelner, ibid., 65, 1804 (1961).

[**] K. J. Mysels and E. K. Mysels, J. Am. Chem. Soc., 83, 2049 (1961).

sulfate, was indeed affected seriously by this surface which catalyzes the hydrolysis of the ester linkage and causes the formation of lauryl alcohol and sulfuric acid. Hence, the results which we published on this subject and which seemed very interesting at the time are probably in error by an undetermined amount. Nevertheless, the method could be used effectively for a number of other surfactants not adsorbed or hydrolyzed by the glass surface.

2. **Light scattering.** In following up some earlier light scattering work in this laboratory we found that precise results required considerable improvements in both the standardization of the equipment and especially in the purification of solutions. It was in this connection that the effect of fritted glass upon the hydrolysis of sodium lauryl sulfate was discovered and finally ways of obviating it were developed (9). This permitted us to obtain highly accurate measurements on solutions of several lauryl sulfates (9), but the technique is so cumbersome and delicate that we did not push it further.

3. **Conductivity measurements.** Both electrophoresis and diffusion measurements required auxiliary determinations of electric conductivity. Later we used these determinations as our primary tool. In the course of this work we gradually improved the design of the cells (16) to a point where measurements of very high precision (of the order of ten ppm) can be performed quite easily and rapidly. The big step here was the "doughnut" design which permits excellent hydrodynamic contact of the measuring area with another reservoir with negligible electric interaction between the two.

Materials

Although there are significant results that can be obtained with impure association colloids, quantitative results and quantitative interpretation generally require materials of high purity. Yet there are no standards, no recognized methods of purification, no criteria of purity that can be depended upon. Hence preparation of pure materials is quite difficult and has consumed much more of our time and effort than would

appear from the brief description in the reports and publications.

Sodium lauryl sulfate. Most of our work was done with sodium lauryl sulfate which was prepared by conventional methods. For many years no difficulties were encountered and a pure material was repeatedly prepared or recovered (3,4,6,10,11,14,15). About 1958, however, an apparently slightly different material was obtained which seemed equally pure but had a slightly different equivalent conductivity below the c.m.c. (17). Despite considerable effort we have been unable to establish the cause of this discrepancy, but we believe that it has little effect on any of our results.

Other lauryl sulfates. We have developed a method for preparing pure silver lauryl sulfate from the sodium salt. This involves a delicate recrystallization over a narrow temperature range (12). From this a variety of other soluble lauryl sulfates, such as those of the alkali metals and of a series of quarternary alkyl ammonium ions, have been prepared by double decomposition with the corresponding halide (12).

Sodium decyl sulfate. The solubility of this salt makes the usual methods of purification almost worthless. We have therefore developed the new approach of recrystallizing the alcoholate to remove all inorganic salts and followed this by extraction of the alcohol with ether which is quite easy (19).

Sodium tetradecyl sulfate. The purification of this material proved unexpectedly difficult. We have spent much time attempting to remove the alcohol by extraction with ether, but found that the extraction was so slow that hydrolysis due to traces of water set in long before it was completed. A variety of recrystallization attempts also led to no result. We are now studying a very promising method, namely, sublimation of the alcohol in high vacuum. The difficulty here is the development of auxiliary techniques which would indicate when sufficient purification has been attained. When sufficiently perfected, this high vacuum method should give us not only the pure tetradecyl sulfate, but also other compounds in a higher degree of purity than heretofore obtainable and in addition provide information about the phase behavior of the alkyl sulfate -alcohol systems (unpublished).

Light Scattering

Results of light scattering measurements on association colloidal
electrolytes were first interpreted by Debye without taking into account
their charge. Later, the effect of the charge upon the extent of fluctua-
tion was taken into account. Soo thereafter, under this project a discus-
sion of the effect of charge upon the optical efficiency of fluctuations
was given in easily visualized terms and along with a discussion of the
effect of the equilibrium between micelles and monomers (7). Almost
simultaneously a somewhat more rigorous treatment of this effect of
charge on optical efficiency was given by Prins and Hermans.[*] We disagreed
with certain minor points in that treatment, and we also needed results
expressed in terms of operational quantities and therefore presented a
final version of this approach (9). Later, details dealing with polydispersed
systems were added (14).

This theory attempts to obtain an accurate molecular weight but only
an effective, thermodynamic charge which is certainly much lower than the
true charge of the particle. Recently, more elaborate treatments have
appeared whose purpose it is to interpret light scattering in terms of the
true weight and the true charge of the particle.[**] It still is not clear
whether the results of these more complicated theories are really different
for the molecular weight while admittedly the values for the charge are
closer to the true value.

The Composition and Thermodynamics of Mixed Micelles

By careful analysis of the significant factors determining the
conductivity of a micellar system we have been able to develop a method
(17) for interpreting the conductivity of mixed systems in terms of the

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[*] W. Prins, Thesis, Leyden, 1955; W. Prins and J. J. Hermans, Proc. Kon.
Neder. Akad. Wet. B59, 298 (1956).

[**] Vrij, Thesis, Utrecht, 1959; D. Stigter, J. Phys. Chem., 64, 842 (1960).

composition of micelles, i.e., of the percentage of the two components present in the micelle. This is a quantity which has not been heretofore available and is required in any evaluation of the interactions that occur inside the micelle. Then in order to evaluate this interaction we clarified the assumptions in prior discussions of the theory of mixed micellization and introduced corrections for nonideality (18). The results were again expressed in operational quantities so as to give a direct evaluation of the experiments. A simple criterion for ideality or nonideality of the monomeric solution bathing the micelles was developed incidentally to this treatment (18).

Micellar Density

The interpretation of kinetic properties of the micelle in terms of its structure and hydration requires a knowledge of the volume occupied by the micelle-forming ions themselves. An analysis of this problem in terms of the best available knowledge about the volumes of individual ions and about electrostriction has been presented (TR 12). Publication of this work has been delayed pending the appearance of supporting references based on some other work of Dr. Mukerjee. Now that these references have been published, Dr. Mukerjee is introducing some further refinements into his manuscript, and it should be resubmitted for publication soon.

Electrodiffusion

Consideration of what happens during electrolysis of a reacting system such as, for example, a micellar system in which the sodium ion is sometimes attached to the micelle and sometimes free, or the water molecules are sometimes moving as part of the hydration shell of an ion and sometimes not, led to the development of the theory of such processes. It turned out that the reaction during electrolysis introduces an additional diffusion effect which was termed "electrodiffusion." Quantitative considerations indicated that it should be possible to measure the reaction

rate by determining this electrodiffusion. This method could have considerable advantages in that it is applicable to quite fast reactions having a half-life of a second or less, yet is to be applied to an equilibrium system and involves experiments which are quite leisurely since what is measured is the diffusion resulting from the reaction process being repeated many, many times (8).

Publication of this theory was followed by several papers from other laboratories[*] and also led to additional work here under an NSF grant.[**] It turns out that, while the original paper contained minor errors, the approach is sound in principle, but that experimental difficulties still remain to be overcome.[***]

The Structure of the Micelle

1. Size and shape. On the basis of light scattering data the molecular weight of the micelle must be of the order of 18,000 corresponding to slightly over 60 monomers aggregating to form the micelle. This refers to the surfactant dissolved in pure water. In the presence of sodium chloride the molecular weight increases reaching about 41,000 in 0.5 M NaCl (14). The data in the presence of sodium chloride seem to be more certain as excellent agreement is obtained between three laboratories. In pure water our results are some 20% higher than the others, but we hope that our results are closer to the truth because of the care with which our standardization was conducted and our material prepared. As indicated above, it is likely that the uncertainty in interpretation is by now very small.

The nature of the counterion has a small effect on the size of the micelle, but this effect is not as pronounced as upon the critical micelle

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[*] Lamm, Acta Chem. Scand., 1956, 10, 1132; Giddings, J. Chem. Phys., 26, 1755 (1957); Ljunggren, Acta Chem. Scand., 12, 1529 (1958); Bak and Kauman, Trans. Faraday Soc., 55, 1109 (1959); Ljunggren, Trans. Roy. Inst. Technol. Stockholm, 1959, 142.

[**] Scholten and Mysels, Trans. Faraday Soc., 56, 994 (1960); Scholten and Mysels, ibid., 57, 764 (1961); Scholten, Arch. Biochem. Biophys., 93, 568 (1961).

[***] Scholten and Mysels, J. Chem. Phys. (in press)(1961).

concentration (8).

The smallness of the micelle thus established makes any lamellar or sandwich structure highly improbable, because the sides or periphery of the lamella would have to have a much greater surface than its two faces. In fact, only about half of the monomers could be hidden inside the lamella, and the other half would have to form its periphery. Both the concentration of charges on the face of the lamella and the exposure of large hydrocarbon areas makes such a structure quite unreasonable. On the other hand, a spherical micelle containing some 60 to 70 monomers has a radius much smaller than the length of a molecule so that there is no difficulty about filling the center of the sphere and giving each tail a great deal of freedom of motion within the micelle.

2. **Charge.** Our measurements of the mobility of the sodium constituent in sodium lauryl sulfate solutions in water, combined with results of conductivity measurements on this system, and of mobility determinations of its micelles by the tracer electrophoresis method, show that the true electrokinetic degree of ionization of the micelle is about 28% (6). This means that for each 100 lauryl sulfate ions aggregated to form a micelle about 72 sodium ions are attached strongly enough to the surface of the micelle not to contribute to conductivity. This is in very close agreement with a completely different interpretation of the electrophoretic mobility of the micelles based on micellar size and the diffused double layer theory of relation between mobility and charge.[*]

The same measurements (6) indicated that the micelle is more ionized at higher concentrations than at low concentrations. Similar effects have already been observed by Hartley and named "retrograde ionization." It is a surprising result because clearly the activity of sodium ion increases with the concentration of sodium lauryl sulfate, and therefore, according to the law of mass action, one would expect a lower degree of ionization. In fact, Hartley tended to consider the effect as an artifact produced by the "heterogeneity" of the solution (concentration electrolyte

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[*] Stigter and Mysels, J. Phys. Chem., 59, 45 (1955).

around the micelle, very diluted one in between).

Very recently, however, we have been able to obtain the conductivity of the micellar component in the presence of high concentrations of salt and find that it is essentially constant, although it should decrease markedly if the degree of ionization remains the same (unpublished). This we feel is a definite proof of the reality of the "retrograde" ionization. The behavior seems somewhat less paradoxical at present because we know that the size of the micelle changes at the same time so that the degrees of ionization cannot be directly compared. However, any good rationale for it still is lacking.

While the above electrokinetic measurements give information about the true charge of the micelle, we have interpreted light scattering results in terms of an effective charge on the basis of which the thermodynamic behavior of the micelles can be explained. This degree of ionization is, as would be expected, lower and of the order of 15-18% (14).

The experimental results on which these calculations are based, particularly the electrokinetic measurements, are considered to be of a much higher order of accuracy than the present-day interpretation. As the theory of the double layer becomes more sophisticated, and it is likely that the use of computers will lead to considerable improvement in the very near future, it is possible that the charges calculated will be revised, and if so, the revision is likely to be upwards. However, the basic finding that the micelle is charged and remains charged at high electrolyte concentrations, but that only a minority of the counterions are ionized, is not likely to be modified.

3. Mixed micelles. We have also confirmed that mixed micelles are formed among homologues such as sodium decyl and dodecyl sulfate and have been able to determine for the first time and quite exactly how the mole fraction in the micelle varies with the mole fraction in the solution. The results show that the system is not ideal and that the deviation from ideality may reach 40%. However, closer analysis shows that at least part of the deviation of the system from ideality is due to the monomers rather than to the micelles.

The c.m.c. region

The c.m.c. is the only concentration at which an equilibrium between micelles and monomers exist and at which the concentration of both is known, that of the micelles being sufficiently small to be considered a constant and that of the monomers (or more exactly, of the unmicellised solute) being equal to the stoichiometric concentration. Hence, changes in the c.m.c. are a sensitive measure of the balance of forces causing the formation of micelles, provided that the changes in the monomeric solution are well understood.

1. Sodium lauryl sulfate and salt. Since interpretation of the experimentally measured behavior of micelles in terms of their structure generally requires extrapolation to conditions under which interaction between the micelles is negligible, i.e., to zero concentration of micelles, we were concerned with establishing this concentration, i.e., the critical micelle concentration, or c.m.c. In order to make sure that this concentration was meaningful, we used three different methods, namely, electrical conductivity, light scattering, and dye solubilization. We found that, while each method had its limitation, they all gave consistent results (4).

These results, however, did not agree with the "spectral change" dye method which was then very popular. Other work has since then shown that the spectral change method involved substantial systematic errors because the dye reacted with the surfactant to form insoluble products which also induced micelle formations at concentrations where pure micelles were unstable.[*]

Our measurements extended from pure water to 0.4 M sodium chloride, and while the values in pure water are now generally accepted, those at high salt concentrations have been challenged.[**] We have therefore returned to the subject very recently with the improved conductivimetric

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[*] Mukerjee and Mysels, J. Am. Chem. Soc., 77, 2937 (1955).

[**] Matijevic and Pethica, Trans. Faraday Soc., 54, 587 (1958).

technique and have been able to confirm unambiguously the essential correctness of our published results in the presence of large concentration of salt (unpublished). These measurements have also led to the surprising discovery that at sufficiently high salt concentrations the conductivity of the micelles becomes the same as that of the monomers so that conductivimetric measurements do not show any change at the c.m.c. at about 0.4 M NaCl (unpublished). Whether an actual reversal can be observed at still higher concentrations has not yet been established.

2. Effect of alcohol. In connection with our light scattering measurements we have also investigated what happens in the c.m.c. region when the most ubiquitous impurity, namely, the alcohol of same chain length is present in small amounts. We confirmed that a tremendous increase in turbidity occurs and found that it is essentially proportional to the amount of alcohol present, so that light scattering represents a very sensitive, though cumbersome, method of determining this impurity. We also found that lauryl alcohol, like other easily solubilized impurities, induces micelle formation appreciably below the c.m.c. of the pure surfactant (15).

3. Effect of counterion. We have measured the effect of changing counterions upon the formation of micelles by lauryl sulfates and found that for the alkali metal ions the c.m.c. decreased from lithium to cesium in a regular manner and by considerably more than was indicated by previous reports in the literature (unpublished). These changes probably indicate that the hydrated ions are less closely attached to the micelle and therefore contribute less to its formation. Measurement of the effect of excess counterions (present as a chloride) showed that the electrostatic interaction is otherwise unchanged (unpublished). This is as would be expected, but was in contrast with some of the data in the literature.

We have also investigated the effect of a more drastic change in the nature of the counterion by using the symmetrical quaternary ammonium salts from tetramethyl to tetra-n-propyl. Here the c.m.c. decreases drastically with the increasing size of the ion, i.e., despite a reduction

of the electrostatic interaction (unpublished). This is also despite
the increasing weakness of these salts below the c.m.c. which reduces the
activity of the monomers and therefore would lead to an increased
stoichiometric c.m.c. It can be explained only by assuming a substantial
non-electrostatic interaction between the micelle and the counterion, and
we see the source of this interaction in the hydrophobic surface of the
counterion and hydrophobic regions on the micelle. Contact at these points
can reduce the hydrocarbon-water interface in the solution.

4. Effect of heavy water. We have also measured the effect of
changing the solvent from water to deuterium oxide and found, rather
surprisingly, no measurable difference (unpublished). This result is
interesting in view of the fact that the net heat of micellisation is
very low, so that entropy must be the main driving force. It has been
postulated[*] that this entropy stems from the reduction in "iceberg" forma-
tion around the monomeric ions. One would expect that the different
strengths of hydrogen bonding in water and deuterium oxide, as evidenced
by the difference in their melting points, would produce a significant
difference in the tendency to form micelles, yet our results show that
this is not the case, so that either the iceberg explanation does not hold
or some compensating effects occur. The fact that we have found no
difference for either the decyl or dodecyl sodium sulfates makes a
fortuitous compensation rather unlikely.

5. In connection with the work on mixed micelles we have determined
very precisely the c.m.c. of mixed sodium decyl and dodecyl sulfates,
confirming the previous findings that, as far as the c.m.c. was concerned,
these two solutes seem to interact in an ideal fashion (17). However,
we have shown also that this is not a sufficient criterion of ideality and
may result from the compensating effects occurring in micelles and in
the monomeric solution (18).

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[*] C. A. J. Hoeve and G. C. Benson, J. Phys. Chem., 61, 1149 (1957).

The Dilute Region

The interpretation of the experimentally observed behavior of micelles requires not only extrapolation to their zero concentration, but also a knowledge of the medium by which they are then bathed. Because of the importance of electrostatic interaction, the number and charge of the ions present is particularly significant. This, and the discrepancy between some of our observations and the literature, led us to an experimental investigation of the behavior of sodium lauryl sulfate and some other surfactants below the c.m.c. and into the most dilute solutions accessible where the interaction between simple ions is better understood.

Dimerization. Measurements of conductance on sodium and lithium lauryl sulfate at concentrations below about 10^{-3} M (which is some 8 times more dilute than the c.m.c.) could only be interpreted in terms of an equilibrium between the simple, fully ionized lauryl sulfate ion, LS^-, and its dimer carrying a double negative charge, $LS_2^=$ (10). This was confirmed by transference measurements conducted in Professor Gordon's laboratory at Toronto where the necessary equipment and know-how was available (11) and by anaanalysis of a number of good measurements in the literature (13).

The formation of such a dimer is not improbable on structural grounds since it permits the charged heads to remain quite far apart while intertwining tails reduce the water hydrocarbon interface in the solution. Its existence affects greatly the interpretation of data around the c.m.c. since it means that divalent ions are present and also that the activity of the stoichiometrically present lauryl sulfate is considerably below unity. However, the methods used could not determine nor predict the concentration of the dimer in the c.m.c. region with the required accuracy, and we are still searching for good methods of accomplishing this.

One way of approaching the problem of what happens in the dilute region is to vary the length of the micelle-forming ion. We have therefore

studied the solutions of the sodium decyl sulfate and found that, as far as conductivity is concerned, they did not show any appreciable deviation from ideality (19). This is somewhat unexpected because it would have been anticipated that dimers would be present, although in a smaller proportion than in the dodecyl sulfate. We have not yet been able to study the tetradecyl sulfate because of the difficulties in its preparation (see above).

2. Weakness. Measurements on lauryl sulfates of silver and several quaternary ammonium compounds showed that these salts were weak, i.e., that in addition to dimerization between similarly charged ions there occurred also ion pair formation between oppositely charged ions (12). This again is not unreasonable in case of the quaternary ammonium compounds because of the hydrophobic surface of these ions which should tend to attract the hydrophobic chain of the lauryl sulfate ion.

Very recently, quite difficult measurements of the absolute conductivity of sodium lauryl sulfate and other salts in the presence of high concentration of NaCl showed that sodium lauryl sulfate does not behave as a simple 1-1 or 1-2 electrolyte. The conductivity of the sodium lauryl sulfate decreases much more rapidly with increasing NaCl concentration. We are tentatively ascribing the results to the weakness of the dimer and an equilibrium involving $NaLS_2^-$ (unpublished). If this is confirmed, it will further complicate the interpretation of the structure of micelles but may finally bring order into the properties of the "monomeric" solution below the c.m.c. and also provide us with some information about the forces acting between the lauryl sulfate ions and counterions which must be of the same nature as those involved in the formation of micelles.

Summary

Thus, work under this project has contributed new techniques, new interpretations, and new data which have considerably clarified the facts about the behavior of solutions of association colloids. These facts show, however, that the picture is not as simple as anticipated and that surprisingly enough, the main difficulty is now not in determining what micelles are doing, but what the "monomers" are doing.

II. PERSONNEL

As has been emphasized by Conant, science is not only the results
contained in books and periodicals, but also a way of thinking and living
of the scientists. It is therefore proper in this report to list not
only the published or publishable results obtained under this contract,
but also to indicate at least briefly the students, research associates,
and research assistants who were supported by it and some of their
activities since. These are in chronological order.

Horst W. Hoyer was supported by this project during the final stages
of his Ph.D. study while developing the tracer electrophoresis methods.
After a short stay in industry he taught first at North Dakota and then
moved to Hunters College where he is now Associate Professor. With the
help of his undergraduate students and of NSF support he has continued an
active research program mainly in colloidal electrolytes. Last year he
spent a year at Berkeley studying modern biochemistry under an NSF Faculty
Fellowship.

Dirk Stigter came here for a year and a half after completing his
preliminary examinations at the University of Utrecht, Holland, to conduct
work towards his thesis to be submitted at that university. He completed
the development of the open tube tracer electrophoresis method and
developed the sintered disc method of measuring diffusion coefficients.
After returning to Holland and obtaining his Ph.D. degree, he spent three
years in the Dutch industry and then returned to the United States, first
as a postdoctoral at the University of Oregon with Professor Terrell Hill,
and now is living in Berkeley, California, working at the Western Regional
Laboratory of the U. S. Department of Agriculture at Albany. He continues
an active research program mainly along theoretical lines on electro-
kinetics, thermodynamics of charged colloidal systems, light scattering, etc.

Robert J. Williams, a student of Professor Barton at University of
London, spent a postdoctoral year on the project studying the diffusion
of sodium lauryl sulfate and also its critical micelle concentration. From

here he moved to a postdoctoral year at the University of Wisconsin in reaction kinetics, and then returned to England where he is now teaching at the University of Exeter.

Cyril I. Dulin, who obtained his Ph.D. with Professor Elton at Battersea Polytechnic Institute in England, spent also a postdoctoral year on the project studying the electrophoretic mobility of the sodium in solutions of sodium lauryl sulfate and also determining its conductivity over a wide range of concentrations. He then took a position with the E. I. du Pont de Nemours Company and spent several years in Wilmington before being transferred to the British branch of the company.

Pasupati Mukerjee was supported by the project through a large part of his Ph.D. studies and then for a postdoctoral year. His work was concerned with the effect of counterions upon the critical micelle concentration, the behavior of dilute solutions, and the calculation of micellar volumes. From here he went for a two-year postdoctoral stay at the Brookhaven National Laboratories, and then returned to India to become a reader at the Institute of the Indian Association for the Cultivation of Science in Calcutta. He has now published two theoretical papers on ionic volumes and entropies and is actively pursuing a research program dealing largely with colloidal electrolytes.

H. L. Princen came here to conduct research work towards his Ph.D. degree, which he received later from the University of Utrecht, Holland. He studied light scattering from a theoretical and experimental point of view. After returning to Holland, where he completed his military service doing mostly research on light scattering, he took a position with the U. S. Department of Agriculture laboratory in Peoria, Illinois, where he conducting research on pigments and emulsions.

Mrs. Paz Kapauan was a part-time research assistant on the project after obtaining her M.S. degree at the University of Southern California and before returning to the Philippines with her husband who is now teaching at the University of the Philippines. She was concerned with precise conductivity measurements and the preparation of several alkali metal lauryl sulfates.

R. J. Otter spent two years as a postdoctoral here after obtaining his Ph.D. from the University of Reading, England. His principal effort was the preparation of sodium decyl, lauryl and tetradecyl sulfates and in the study of the mixed micelles of sodium decyl and dodecyl sulfates. He has now returned to England to a research position with Imperial Chemical Industries at Billingham.

Saulé Liulevicius Palubinskas has begun her study towards a M.S. degree with the support of this project. She is a graduate of Mundelein College in Chicago where during her junior year she won the first prize in the essay category of the Continental Oil Company Contest in Colloid and Surface Chemistry for 1959. Her research is concerned with the high vacuum purification of sodium tetradecyl sulfate and the behavior of its alcoholate.

Dr. Estella K. Mysels has been for a short time a postdoctoral research associate on a part-time basis under the project and has been studying the conductivity of sodium lauryl sulfate in high NaCl concentrations.

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The great effect that continued support during the early stages of his academic career had on the principal investigator can perhaps be best indicated by the fact that several grants and contracts that have supported his research since were concerned with work originating under the present contract. These are an NIH grant for the study of serum albumin by tracer electrophoresis, an NSF grant for the development of electrodiffusion, and to a considerable extent a PRF grant and an OSR contract for the study of soap films. Another important effect of the contract was that it gave him the invaluable opportunity to associate with and learn from these collaborators on the project.

III. LIST OF PUBLICATIONS

(1) K. J. Mysels and D. Stigter, "A New Method of Measuring Diffusion Coefficients," J. Phys. Chem., 57, 104 (1953); based on T. R. 1.

(2) H. W. Hoyer, K. J. Mysels, and D. Stigter, "Tracer Electrophoresis. I. Free Liquid Method," J. Phys. Chem., 58, 385 (1954); distributed as T. R. 2.

(3) D. Stigter, R. J. Williams, and K. J. Mysels, "Micellar Self Diffusion of Sodium Lauryl Sulfate," J. Phys. Chem., 59, 330 (1955); distributed as T. R. 4.

(4) R. J. Williams, J. N. Phillips, and K. J. Mysels, "The Critical Concentration of Sodium Lauryl Sulfate at 25°C.," Trans. Faraday Soc., 51, 728 (1955); distributed as T. R. 3.

(5) K. J. Mysels and H. W. Hoyer, "Tracer Electrophoresis. IV. Modified Brady Method," J. Phys. Chem., 59, 1119 (1955); distributed as T. R. 7.

(6) K. J. Mysels and C. I. Dulin, "Tracer Electrophoresis. III. The Mobility of the Na^+ Constituent in Sodium Lauryl Sulfate Solutions," J. Colloid Sci., 10, 461 (1955).

(7) K. J. Mysels, "Charge Effects in Light Scattering by Association Colloidal Electrolytes," J. Colloid Sci., 10, 507 (1955); with tables distributed as T. R. 8.

(8) K. J. Mysels, "Electrodiffusion: A Fluctuation Method for Measuring Reaction Rates," J. Chem. Phys., 24, 371 (1956); distributed as T. R. 6.

(9) L. H. Princen and K. J. Mysels, "Light Scattering by Ideal Colloidal Electrolytes," J. Colloid Sci., 12, 594 (1957); distributed as T. R. 9.

(10) P. Mukerjee, K. J. Mysels, and C. I. Dulin, "Dilute Solutions of Amphipathic Ions. I. Conductivity of Strong Salts and Dimerization," J. Phys. Chem., 62, 1390 (1958); manuscript distributed as part of T. R. 10.

(11) P. Mukerjee, "Dilute Solutions of Amphipathic Ions. II. Transference of Lauryl Sulfate in Sodium Lauryl Sulfate," J. Phys. Chem., 62, 1397 (1958); manuscript distributed as part of T. R. 10.

(12) P. Mukerjee and K. J. Mysels, "Dilute Solutions of Amphipathic Ions. III. Conductivity of Weak Salts," J. Phys. Chem., 62, 1400 (1958); manuscript distributed as part of T. R. 10.

(13) P. Mukerjee, "Dilute Solutions of Amphipathic Ions. IV. Some General Effects of Dimerization," J. Phys. Chem., 62, 1404 (1958); manuscript distributed as part of T. R. 10.

(14) K. J. Mysels and L. H. Princen, "Light Scattering by Some Lauryl Sulfate Solutions," J. Phys. Chem., 63, 1696 (1959); manuscript and details of experimental procedures and calculations distributed as part of T. R. 11.

(15) L. H. Princen and K. J. Mysels, "Some Effects of Lauryl Alcohol on Light Scattering by Sodium Lauryl Sulfate Solutions," J. Phys. Chem., 63, 1781 (1959); manuscript and details of experimental procedures and calculations distributed as part of T. R. 10.

(16) K. J. Mysels, "Improvements in the Design of Conductivity Cells," J. Phys. Chem., 65, 1081 (1961); manuscript distributed as T. R. 13.

(17) K. J. Mysels and R. J. Otter, "Conductivity of Mixed Sodium Decyl and Dodecyl Sulfates -- The Composition of Mixed Micelles," J. Colloid Sci., 16, 462 (1961); manuscript and tables of data distributed as part of T. R. 14.

(18) K. J. Mysels and R. J. Otter, "Thermodynamic Aspects of Mixed Micelles --Application to an Empirically Established Equilibrium," J. Colloid Sci., 16, 474 (1961); manuscript and tables of data distributed as part of T. R. 14.

(19) K. J. Mysels and P. Kapauan, "Electric Conductivity of Sodium Decyl Sulfate Solutions," J. Colloid Sci., 16, 481 (1961); manuscript and tables of data distributed as part of T. R. 14.

Related publications: The following article is closely related to work on this project: K. J. Mysels, "Tagging the Elusive Micelle," Research Reviews, Sept., 1953, p. 15.

Future publications: The following material, described in Section I, is ready for publication, but the manuscripts have not yet been prepared.

       A. "Micellar density," by P. Mukerjee. The original manuscript formed T. R. 12 and is now being revised radically.

       B. "The effect of counterions on the critical micelle concentration," by P. Mukerjee, K. J. Mysels, and P. Kapauan. Part of this material is in P. Mukerjee's thesis (USC, 1957), and it is hoped that the whole will be written up in the near future.

       C. "The effect of deuterium oxide on the critical micelle concentration," by P. Mukerjee and P. Kapauan. It is hoped that this will be written up soon.

The following material, also described in Section I, is not yet complete enough to plan a manuscript, but presumably will reach that stage within a year or so:

       D. "Purification of alkyl sulfates by a high vacuum technique," by K. J. Mysels and S. Palubinskas.

       E. "Conductivimetric studies of sodium lauryl sulfate in the presence of NaCl," E. K. Mysels and K. J. Mysels.

IV. TECHNICAL REPORTS

T. R. 1 - New Method of Determining Diffusion Coefficients.

  K. J. Mysels and D. Stigter, June 1952.

  Published in part as paper (1).

T. R. 2 - Tracer Electrophoresis. I. Free Liquid Method.

  H. W. Hoyer, K. J. Mysels, and D. Stigter, June 1954.

  Published in part as paper (2).

T. R. 3 - The Critical Micelle Concentration of Sodium Lauryl Sulfate at 25°C.

  R. J. Williams, J. N. Phillips, and K. J. Mysels, May 1955.

  Published as paper (4).

T. R. 4 - Micellar Self Diffusion of Sodium Lauryl Sulfate.

  D. Stigter, R. J. Williams, and K. J. Mysels, May 1955.

  Published as paper (3).

T. R. 5 - Tracer Electrophoresis. III. The Mobility of the Na^+ Constituent in Sodium Lauryl Sulfate Solutions.

  K. J. Mysels and C. I. Dulin, October 1955.

  Published as paper (6).

T. R. 6 - Electrodiffusion: A Fluctuation Method for Measuring Reaction Rates.

  K. J. Mysels, February 1956.

  Published as paper (8).

T. R. 7 - Tracer Electrophoresis. IV. Modified Brady Method.

  K. J. Mysels and H. W. Hoyer, October 1955.

  Published as paper (5).

T. R. 8 - Charge Effects in Light Scattering by Association Colloidal Electrolytes.

  K. J. Mysels, December 1955.

  Published as paper (7).

T. R. 9 - Light Scattering by Ideal Colloidal Electrolytes.

> L. H. Princen and K. J. Mysels, February 1958.
> Published as paper (9).

T. R. 10 - Dilute Solutions of Amphipathic Ions, September 1957.

> I. Conductivity of Strong Salts and Dimerisation.
>> P. Mukerjee, K. J. Mysels, and C. I. Dulin.
> II. Transference of Lauryl Sulfate in Sodium Lauryl Sulfate.
>> P. Mukerjee.
> III. Conductivity of Weak Salts.
>> P. Mukerjee and K. J. Mysels.
> IV. Some General Effects of Dimerization.
>> P. Mukerjee.
> Published as papers (10), (11), (12) and (13).

T. R. 11 - Light Scattering by Solutions of Lauryl Sulfates.

> K. J. Mysels and L. H. Princen, September 1958.
> Published as paper (11).

T. R. 12 - Density of Micelles of Association Colloidal Electrolytes.

> P. Mukerjee, January 1959.

T. R. 13 - Improvements in the Design of Conductivity Cells.

> K. J. Mysels, August 1960.
> Published as paper (16).

T. R. 14 - Conductivimetric Studies in the Sodium Decyl-Dodecyl Sulfates System, October 1960.

> I. Conductivity of Mixed Sodium Decyl and Dodecyl Sulfates
>> -- The Composition of Mixed Micelles.
>> K. J. Mysels and R. J. Otter.
> II. Thermodynamic Aspects of Mixed Micelles -- Application to an Empirically Established Equilibrium.
>> K. J. Mysels and R. J. Otter.
> III. Electric Conductivity of Sodium Decyl Sulfate Solutions.
>> K. J. Mysels and P. Kapauan.
> Published as papers (17), (18), and (19).

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